

# Sulfur biogeochemistry and isotopic fractionation in shallow groundwater and sediments of Owens Dry Lake, California

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## Abstract

Groundwater and sediment samples (~1 m depth) at sites representative of different groundwater pathways were collected to determine the aqueous speciation of sulfur and the fractionation of sulfur isotopes in aqueous and solid phases. In addition, selected sediment samples at 5 depths (from oxic to anoxic layers) were collected to investigate the processes controlling sulfur biogeochemistry in sedimentary layers. Pyrite was the dominant sulfur-bearing phase in the capillary fringe and groundwater zones where anoxic conditions are found. Low concentrations of pyrite ( $<5.9 \text{ g kg}^{-1}$ ) coupled with high concentrations of dissolved sulfide ( $4.81$  to  $134.7 \text{ mg L}^{-1}$ ) and low concentrations of dissolved Fe (generally  $<1 \text{ mg L}^{-1}$ ) and reducible solid-phase Fe indicate that availability of reactive Fe limits pyrite formation. The relative uniformity of down-core isotopic trends for sulfur-bearing mineral phases in the sedimentary layers suggests that sulfate reduction does not result in significant sulfate depletion in the sediment. Sulfate availability in the deeper sediments may be enhanced by convective vertical mixing between upper and lower sedimentary layers due to evaporative concentration. The large isotope fractionation between dissolved sulfate and sedimentary sulfides at Owens Lake provides evidence for initial fractionation from bacterial sulfate reduction and additional fractionation generated by sulfide oxidation followed by disproportionation of intermediate oxidation state sulfur compounds. The high salinity in the Owens Lake brines may be a factor controlling sulfate reduction and disproportionation in hypersaline conditions and results in relatively constant values for isotope fractionation between dissolved sulfate and total reduced sulfur.

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## 1. Introduction

Many studies have investigated sulfur cycling in marine sediments (e.g., Lyons and Berner, 1992; Mossman et al., 1991; Henneke et al., 1997; Sternbeck and Sohlenius, 1997), but there have been relatively few studies of sulfur biogeochemistry under anoxic, hyper-

saline conditions (e.g., Brandt et al., 2001; Gavrieli et al., 2001; Ingvorsen and Brandt, 2002). Sulfur biogeochemistry is often an important regulator of redox chemistry under these conditions and has strong linkages with nutrient cycling, groundwater chemistry, trace-metal redox behavior, microbiological energetics, and mineralogical composition of sediments. We were particularly interested in the sulfur biogeochemistry of shallow groundwater and sediments at Owens Dry Lake, because it has important ramifications for efforts underway to mitigate dust generation from the dry

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lakebed through establishment of native vegetation. Previous research indicated that shallow anoxic groundwater was a major limitation for the establishment of vegetation on the Owens playa (Dahlgren et al., 1997). Shallow groundwaters are often present within the upper 80 cm of sediment and have the following chemical characteristics: EC up to  $171 \text{ dS m}^{-1}$ ,  $E_h \approx -230 \text{ mV}$  and  $\text{pH} \approx 9.6$ .

Dust produced from the dry lakebed is partially derived from salts formed by evaporation of hypersaline groundwater that often contains high concentrations of potentially toxic trace elements (Reid et al., 1994). For example, As(III) (up to  $96 \text{ mg L}^{-1}$ ) is the predominant form of arsenic in shallow groundwater due to the strongly reducing conditions (Ryu et al., 2002). As(III) is more soluble, less strongly adsorbed, and more toxic than As(V) resulting in several environmental and human-health concerns in the vicinity of Owens Dry Lake. A previous study also indicated that sulfate reduction is the major process regulating redox conditions in the shallow groundwater over the majority of the dry lakebed (Ryu et al., 2004).

Processes involving sulfur biogeochemistry in natural environments are complex and include microbial sulfate reduction (Goldhaber and Kaplan, 1975; Jørgensen, 1982; Albert et al., 1995), precipitation of sulfur-bearing solid phases such as pyrite ( $\text{FeS}_2$ ), acid volatile sulfide (Berner, 1970, 1984), gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) and other sulfates (Holser and Kaplan, 1966), and sulfide oxidation and subsequent disproportionation (Jørgensen, 1990; Canfield and Thamdrup, 1994). Aqueous speciation and solid-phase sulfur fractionation coupled with sulfur isotopic composition have been used to effectively interpret sulfur biogeochemical processes (Calvert et al., 1996; Sternbeck and Sohlenius, 1997; Passier et al., 1999). Sulfur consists largely of two stable isotopes,  $^{32}\text{S}$  and  $^{34}\text{S}$ , which have natural abundance of 95.02% and 4.21%, respectively (Hoefs, 1997). Bacterial sulfate reduction results in the depletion of  $^{32}\text{S}$  in the remaining dissolved sulfate and the enrichment of  $^{32}\text{S}$  in sulfide (Kaplan and Rittenberg, 1964; Goldhaber and Kaplan, 1975). The preference for  $^{32}\text{S}$  by sulfate reducers is due to the lower bond strength of  $^{32}\text{S}-\text{O}$  compared to  $^{34}\text{S}-\text{O}$  (equilibrium fractionation), and faster reaction kinetics for the lighter isotopes (kinetic fractionation) (Clark and Fritz, 1997).

The magnitude of the isotopic separation between sulfate and sulfide due to bacterial sulfate reduction in culture experiments has been observed to be inversely proportional to the specific rate (rate per cell) of sulfate reduction (Kaplan and Rittenberg, 1964; Habicht et al., 1998). However, laboratory cultures of sulfate reducing

bacteria show a large range (2–47‰) of fractionation between sulfate and sulfide (Kaplan and Rittenberg, 1964; Bolliger et al., 2001; Detmers et al., 2001). Natural samples of reduced sediments show an even larger range in the isotopic difference between pore water sulfate and diagenetic iron sulfide. Isotopic fractionations as large as 60–70‰ are observed (Goldhaber and Kaplan, 1980), which are well in excess of values expected from single stage bacterial sulfate reduction. The extremely light sulfides in field conditions has been proposed to result from the considerably slower sulfate reduction rates in natural environments compared to those under laboratory conditions (Trudinger and Chambers, 1973; Rees, 1973; Goldhaber and Kaplan, 1980). More recent work has also shown that partial oxidation of reduced sulfur ( $\text{H}_2\text{S}$ ) to intermediate oxidation states (elemental sulfur, sulfite, thiosulfate), followed by disproportionation into sulfide and sulfate results in significant isotope fractionations and is largely responsible for the most isotopically depleted iron sulfide observed in reduced sediments (Jørgensen, 1990; Canfield and Thamdrup, 1994; Habicht and Canfield, 2001). Therefore, interpretation of sulfur isotope composition may be complicated when  $^{34}\text{S}$ -depleted sulfide produced by sulfate reduction diffuses upward to the oxic or suboxic zone where it can be reoxidized by sulfur oxidizing bacteria.

The precipitation of pyrite is generally the end product of sulfur diagenesis, and is an important part of the sulfur biogeochemical cycle (Berner, 1970, 1984). A powerful tool for interpreting the mechanism of pyrite formation involves coupling the concentration of various forms of sulfur-bearing phases with their sulfur isotope composition (Goldhaber and Kaplan, 1975; Chambers, 1982; Schidlowski et al., 1983). Pyrite formation is generally proposed to require progressive sulfidation of a series of metastable iron sulfides with elemental sulfur ( $\text{S}^0$ ) (Berner, 1970) or polysulfides ( $\text{S}_x^{2-}$ ) (Rickard, 1975; Luther, 1991). The initial precipitation of amorphous  $\text{FeS}$  results from the reaction of dissolved  $\text{Fe(II)}$  with hydrogen sulfide produced by sulfate reduction. The successive sulfidation is believed to undergo the following transformation sequence in formation of pyrite:  $\text{FeS(am)}$  ( $\text{FeS}_{0.90}$  to  $\text{FeS}_{0.92}$ )  $\rightarrow$  mackinawite ( $\text{FeS}_{0.93}$  to  $\text{FeS}_{0.96}$ )  $\rightarrow$  greigite ( $\text{Fe}_3\text{S}_4$ )  $\rightarrow$  pyrite ( $\text{FeS}_2$ ) (Ward, 1970; Sweeney and Kaplan, 1973; Schoonen and Barnes, 1991; Langmuir, 1997).

The objectives of this study were to characterize aqueous and solid-phase sulfur species and to investigate the processes regulating sulfur biogeochemistry in the anoxic, hypersaline shallow groundwater and sediments of Owens Dry Lake. We examined aqueous

speciation and solid-phase fractionation of sulfur combined with sulfur isotope compositions to distinguish transformation pathways. We discuss the effects of the shallow groundwater on sulfur dynamics in the sediment layers and possible factors controlling sulfur biogeochemistry in the groundwater of Owens Dry Lake.

## 2. Study site

Owens Lake is the terminus of the Owens River located in central California ( $36^{\circ} 30' \text{ N}$ ,  $118^{\circ} 00' \text{ W}$ ; Fig. 1). The lake became essentially dry by 1921 because of large diversions of water from the Owens

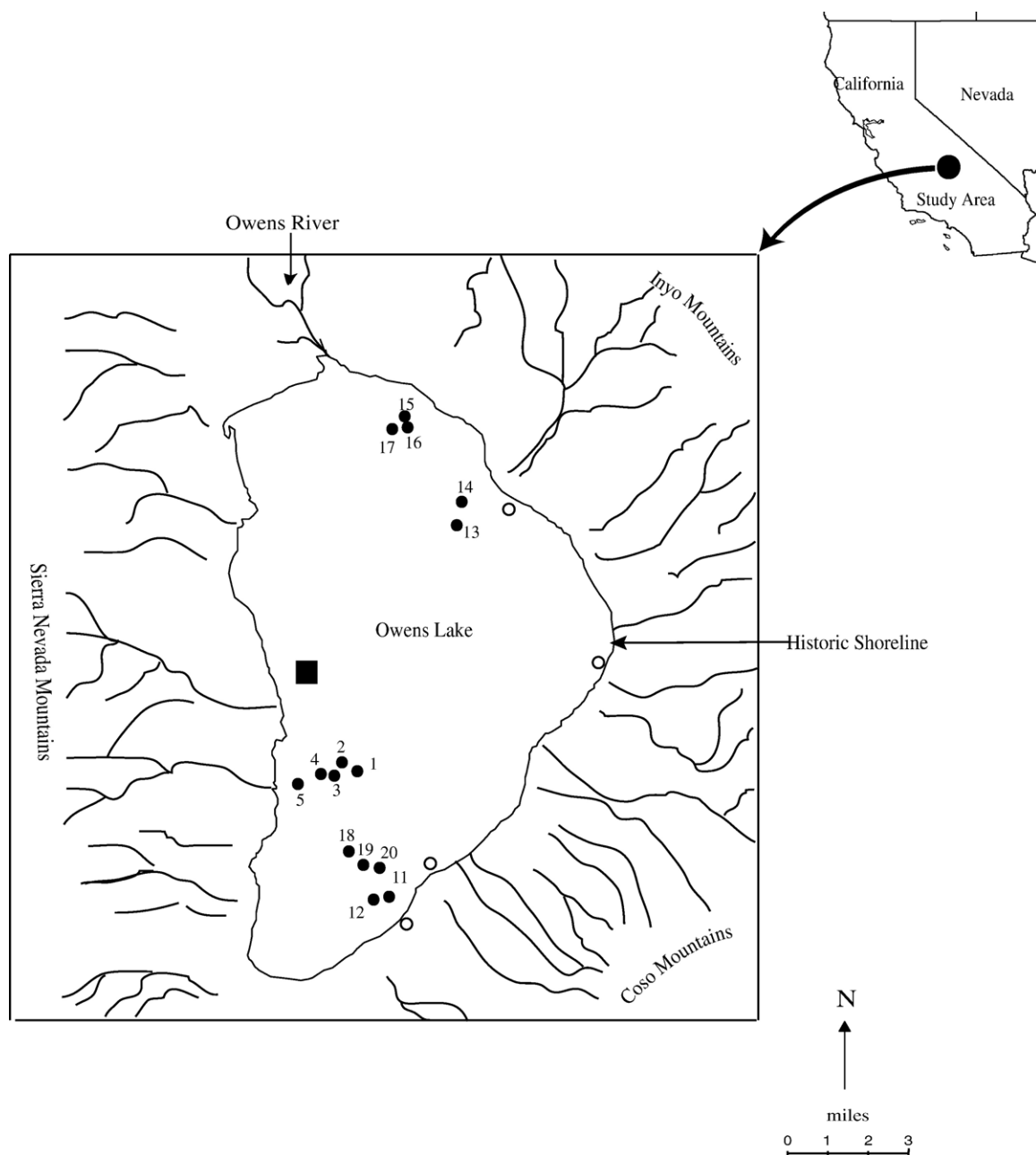


Fig. 1. Location of Owens Dry Lake and sampling sites (●) for sulfur speciation and isotope study. Number indicates sample ID. Groundwater and subsurface sediment samples (~1 m depth) were collected at sites 11–20. Selected sediment at 5 different depths and groundwater samples were collected at sites 1–5. Lopes (1988) showed location of the brine pool (■) and spring zones (○).

River for local irrigation and remote urban use (Kohen et al., 1994). Estimated average summer and winter temperatures are 27 and 3 °C, respectively (Hollet et al., 1991). Mean annual precipitation at Owens playa is estimated to be 100 to 140 mm (Lopes, 1988). Evaporation is the major hydrologic loss from Owens playa with transpiration from plants in wetlands along the lakebed margins a minor hydrologic loss. Estimated evaporation ranges from 88 to 104 mm yr<sup>-1</sup> for the playa surface to 872 mm yr<sup>-1</sup> for the brine covered areas in the west-central portion of the lakebed (Tyler et al., 1997). Groundwater recharge occurs through direct

precipitation on the lakebed, runoff from the surrounding mountains, subsurface flow from the upper Owens Valley and surrounding mountains, and periodic inflow from the Owens River. Evaporative losses concentrate groundwater solute concentrations and lead to formation of surface salt crusts over parts of the lakebed. The analyses of salt crust indicate that the most important crust-forming minerals are halite, natron, thermonatrite, thenardite, mirabilite, and trona (Friedman et al., 1976). The salt crusts on the south and east portions of lakebed were often thin (about 50 mm) and friable and generally porous. In the west-

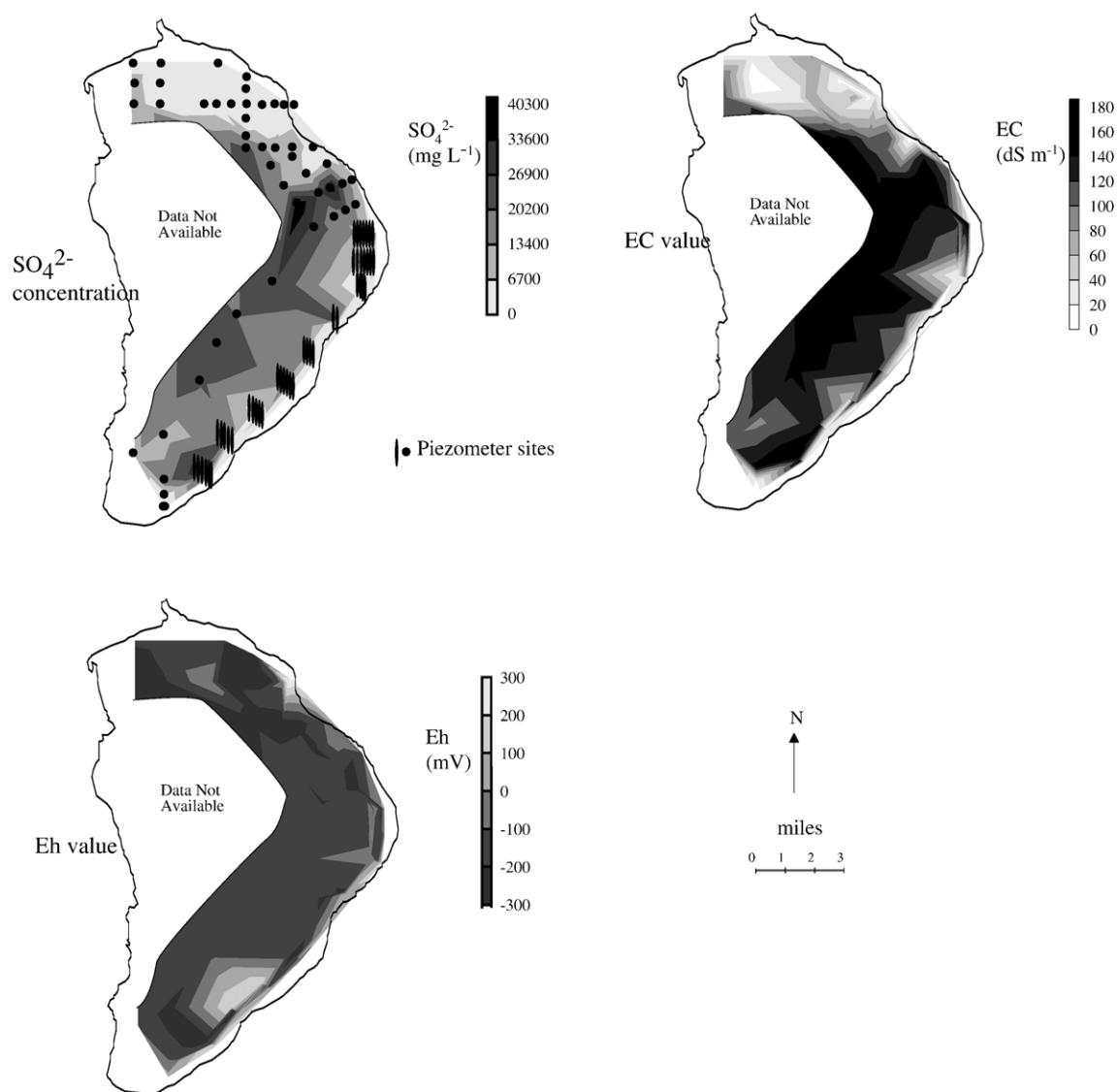


Fig. 2. Contour plot of average dissolved  $\text{SO}_4^{2-}$  concentrations ( $\text{mg L}^{-1}$ ), electrical conductivity (EC) ( $\text{dS m}^{-1}$ ) and redox potential (Eh) (mV) in shallow groundwater at 1 m depth in piezometers for Owens Lake, 1992–1993. No data were collected in areas where the surface was covered by a brine pool. Data were contoured using Delta Graph 4.0.

central portion of Owens Lake, which represents the deepest portions of the pre-diversion lake, trona, mirabolite and halite are present and their thickness can be as much as 3 m (Saint-Amand et al., 1986). The northern portion of Owens Lake was dominantly covered by coarse sand.

Lopes (1988) showed that springs outcrop along the margins of the lakebed where permeable alluvial fan materials contact less permeable lake sediments (Fig. 1). The springs discharge mostly along the southern, east-central and northeastern portions of the lake margin (Lopes, 1988). The groundwater recharged at higher elevations from the Inyo Mountains and Coso Mountain Ranges (Fig. 1) is the source of the spring water (Lopes, 1988) and can influence the distribution of sulfate concentration shown in Fig. 2. The Sierra Nevada Mountains receive the majority of the precipitation and produce the most runoff and subsurface recharge in Owens Valley (Pretti and Stewart, 2002). Sierra Nevada waters provide surface and subsurface waters along the western margin of the lakebed and surface waters for the Owens River, which has a large influence on the northern portion of the lakebed. Sulfate concentration measured in the Owens River in 1965 was  $17 \text{ mg L}^{-1}$  (Friedman et al., 1976). The precipitation contribution of sulfate to streams from the Owens Valley was estimated to be about 1% of the total (Pretti and Stewart, 2002). Inflows from the Owens River in the northern portion of the lake resulted in lower sulfate concentrations of groundwater (Fig. 2).

### 3. Study methods

#### 3.1. Field sampling

The general characteristics of shallow groundwater at Owens Lake were determined from the Great Basin Unified Air Pollution Control District (GBAPCD) piezometer network in fall 1992, spring 1993 and fall 1993. Dissolved sulfate ( $\text{SO}_4^{2-}$ ) concentration, electrical conductivity (EC), and redox potential (Eh) were measured for each of the 92 piezometers monitored at 1 m depth (Fig. 2). The piezometer network was restricted to the eastern portion of the lakebed, because a brine pool in the west-central portion restricted access. Field measurements including EC and Eh were performed immediately upon collection. Samples were sealed in high-density polyethylene (HDPE) bottles and transferred at  $3^\circ\text{C}$  to the laboratory for further analysis.

To analyze sulfur-bearing solid phases and isotopic composition, groundwater and sediment samples were

collected from a depth of 1 m at 10 sites (sites 11–20) (Fig. 1) in July 2000. Another set of sediment and groundwater samples were collected in May 2002 at 5 sites (sites 1–5) from the shoreline toward the center of the lakebed (Fig. 1). At this time, sediment samples were collected from 5 depths: surface crust, unsaturated zone (10 cm below surface crust), capillary fringe, groundwater 1 (upper 20 cm of groundwater) and groundwater 2 (groundwater at about 150 cm depth) (Fig. 4 shows sampling locations and sediment profile at each site). Sediment samples were collected using a bucket auger. The outer portions of the recovered cores were removed with a stainless steel blade to minimize contamination from the corer. Samples were placed in glass jars, flushed with ultra-high purity  $\text{N}_2$  (UHP- $\text{N}_2$ ), and sealed with air-tight caps. All samples were stored in the dark at  $3^\circ\text{C}$  through completion of analysis.

Groundwater samples were collected from wells (7.6 cm diameter  $\times$   $\sim 1.5$  m depth) constructed with a bucket auger. A slotted PVC pipe was immediately placed in the hole and groundwater was pumped using a peristaltic pump ( $\sim 2 \text{ L min}^{-1}$ ). Flow-through cells were installed to monitor dissolved oxygen (DO) and Eh values. After constant DO and Eh values were obtained, water samples were collected for analysis. A YSI Model 54A oxygen meter with a DO probe (Yellow Spring Instrument Inc., Yellow Springs, OH) was used to measure DO. A Sensorex combination ORP electrode (Sensorex Co., Garden Grove, CA) was used to monitor Eh. Depth to groundwater, pH, EC, temperature, and sulfide concentration were measured immediately in the field. A Piccolo pH meter (Hanna instruments, Woonsocket, RI) was used to measure pH. A YSI Model 32 conductance meter was used to determine EC and temperature. Sulfide concentration was determined by ion selective electrode (Model 9416-Orion Research Inc., Beverly, MA). Sulfide antioxidant buffer solution was added to water samples in the ratio of 1:1 prior to the measurement. The electrode was calibrated by serial standards and used to determine concentrations of samples. Ionic strength of the standards was adjusted with 5M  $\text{NaNO}_3$  to be similar to samples. The detection limit of the sulfide measurement was  $0.3 \text{ mg L}^{-1}$ .

Water samples were filtered through a  $0.2\text{-}\mu\text{m}$  membrane filter. For sulfur isotope analysis, a 30-mL HDPE bottle of groundwater was fixed with Zn-acetate to preserve dissolved sulfide as  $\text{ZnS}$ . A second 30-mL bottle of groundwater was acidified with HCl and fixed with  $\text{BaCl}_2$  to preserve dissolved sulfate as  $\text{BaSO}_4$ . Water samples for major cations and anions



were sealed in 125-mL HDPE bottles. For Fe and Mn analysis, ~1% (vol./vol.) concentrated HCl was added to a subsample.

### 3.2. Laboratory methods

Major cation and anion concentrations were determined using a Dionex 4500 ion chromatograph with CS 12 and AS4A separator columns, respectively, and auto-regeneration and conductivity detection (Dionex Co., Sunnyvale, CA). Alkalinity is reported as equivalent  $\text{mg L}^{-1}$  of  $\text{CaCO}_3$  and was determined by acid titration to an endpoint of  $\text{pH}=4.5$  and corrected for the contribution from other species (e.g., boron) using SOLMINEQ.88 (Kharaka et al., 1988). The boron concentration was measured using the azomethine-H colorimetric method (Bingham, 1982). Total Mn concentration was measured using atomic absorption spectroscopy (AAS). The ferrozine method was used to determine Fe(II) and Fe(III) (Stookey, 1970); however, Fe(III) concentrations were generally less than detection ( $<0.01 \text{ mg L}^{-1}$ ). Dissolved organic carbon concentration was measured using a DC-180 carbon analyzer (Dohrmann: Rosemount Analytical Inc., Mason, OH). Organic matter concentrations in sediments were determined by potassium dichromate oxidation of organic carbon and subsequent spectrophotometric measurement (modified Walkley-Black; reproducibility =  $\pm 8\%$ ) (Nelson and Sommers, 1982).

#### 3.2.1. Sulfur extraction method

Fresh sediment samples from the 5 sites (sites 1–5) were processed to estimate concentrations of acid volatile sulfide (AVS), pyrite, sulfate, organic and total sulfur. Separation methods are modified from those described by Canfield et al. (1986) and Tuttle et al. (1986). Sample portions were weighed and then sealed in a glass reaction vessel that was continuously flushed with nitrogen gas. The procedure consisted of first heating the sample in 25 ml of 6M HCl in the reaction vessel, thereby releasing AVS as  $\text{H}_2\text{S}$ . AVS was collected as silver sulfide using a 5 wt.% silver nitrate trap. Following separation of AVS, pyrite was recovered as silver sulfide after reduction with 1M chromous chloride/6M HCl. The residual fraction in the reaction vessel was then filtered through a  $0.4 \mu\text{m}$  filter. Saturated aqueous bromine was added to the filtrate to oxidize any residual organic matter, and then sulfate in the filtrate was recovered by precipitation with barium (Bates et al., 1993). This fraction is dominantly derived from sulfate minerals in samples from the unsaturated zone, but also includes the small amount

of sulfate from residual porewater in samples from the saturated zone. Weight percents of sulfur compounds were calculated gravimetrically from the mass of silver sulfide or barium sulfate collected and the initial sample weight. The repeatability determined by running three replicate samples was found to be within  $\pm 5\%$  for each step. Total sulfur was determined by nitric acid/hydrogen peroxide microwave digestion (Sah and Miller, 1992) with quantification by inductively coupled plasma atomic emission spectrometry (ICP-AES) (Meyer and Keliher, 1992). The detection limit for total sulfur was  $10 \text{ mg kg}^{-1}$ . Organic sulfur was calculated by subtracting AVS, pyrite and sulfate concentrations from total sulfur concentration. Fresh sediments collected in July 2000 (sites 11–20) were assayed for total reduced sulfur (mainly AVS+pyrite) by skipping the AVS separation procedure.

#### 3.2.2. Sulfur isotopes

Precipitates of zinc sulfide ( $\text{ZnS}$ ) and barium sulfate ( $\text{BaSO}_4$ ) from groundwater samples and silver sulfide ( $\text{Ag}_2\text{S}$ ) and barium sulfate ( $\text{BaSO}_4$ ) from the sediment extractions were analyzed for sulfur isotope composition. Sulfur isotope ratios were determined using an Isoprime<sup>®</sup> gas-source, isotope-ratio mass spectrometer interfaced to an automated Carlo Erba<sup>®</sup> elemental analyzer. Samples containing approximately one to two micromoles of sulfur were weighed into tin capsules.  $\text{Ag}_2\text{S}$ ,  $\text{ZnS}$  or  $\text{BaSO}_4$  were combusted in the elemental analyzer in a stream of high purity oxygen to convert the sulfur to  $\text{SO}_2$ . The  $\text{SO}_2$  is carried by a helium stream through a chromatographic column to separate it from other gases and introduced into the isotope ratio mass spectrometer. The sample isotope ratio is determined relative to a pulse of high purity reference gas injected into the mass spectrometer just prior to the arrival of the  $\text{SO}_2$  pulse from the chromatography column. Isotope ratios were reported relative to Canyon Diablo Troilite (CDT) using IAEA reference materials S-1, S-2, S-3 with accepted values of  $-0.3\text{‰}$ ,  $22.67\text{‰}$ , and  $-32.55\text{‰}$ , respectively (Ding et al., 2001). Repeated analyses of laboratory working standards gave an average precision of  $\pm 0.3\text{‰}$  ( $1\sigma$ ).

#### 3.2.3. Aqueous speciation model

Ion activity coefficients and speciation in high ionic strength solutions were determined using SOLMINEQ.88, a geochemical equilibrium model using the Pitzer equation (Kharaka et al., 1988). Mineral saturation indices (SI) of iron sulfide phases were calculated from the ion activity product (IAP) and the equilibrium constant ( $K_{\text{eq}}$ ) for the given mineral:  $\text{SI} = \log [\text{IAP}/$

Table 1

Reactions and Log  $K^\circ$  values at standard states (298.15 °K, 1 bar pressure) used to calculate saturation indices of iron sulfide phases (Langmuir, 1997) and minimum, maximum, and median values of saturation indices of iron sulfide phases examined in this study

Reaction	Log $K^\circ$	Saturation index		
		Minimum	Maximum	Median
$\text{FeS(am)} + \text{H}^+ = \text{Fe}^{2+} + \text{HS}^-$	−2.96	0.9	4.4	3.2
$\text{FeS(mackinawite)} + \text{H}^+ = \text{Fe}^{2+} + \text{HS}^-$	−3.69	1.6	5.2	3.9
$1/3 \text{ Fe}_3\text{S}_4 \text{ (griegite)} + \text{H}^+ = \text{Fe}^{2+} + \text{HS}^- + 1/3 \text{ S}^0$	−4.28	2.2	5.8	4.5
$\text{FeS}_2 \text{ (pyrite)} + \text{H}^+ = \text{Fe}^{2+} + \text{HS}^- + \text{S}^0$	−16.38	14.3	17.9	16.6
$\text{FeS}_2 \text{ (marcasite)} + \text{H}^+ = \text{Fe}^{2+} + \text{HS}^- + \text{S}^0$	−16.05	14.0	17.5	16.2

$K_{\text{eq}}$ ]. Solute activities were obtained from the model computation and solubility data for iron sulfide minerals were acquired from thermodynamic data available from Langmuir (1997; Table 1) ( $\text{pK}_{\text{H}_2\text{S}}=7.00$ ,  $\text{pK}_{\text{HS}}=17.00$  used in SOLMINEQ.88).

## 4. Results and discussion

### 4.1. Spatial patterns for sulfate, EC and Eh in shallow groundwater

Samples collected from the GBAPCD piezometer network show a clear trend of increasing EC values and sulfate concentrations toward the center of the lakebed with lower concentrations along lake margins (Fig. 2). EC values ranged from 5.1 to 171.5  $\text{dS m}^{-1}$  and dissolved sulfate concentration ranged from 0.3 to 40,057  $\text{mg L}^{-1}$ . This pattern for EC and sulfate concentrations appears to be due to variable recharge with fresher water (surface runoff and groundwater flows) along the shorelines.

Friedman et al. (1976) studied chemical evolution of waters from the 1969 flooding of Owens River and subsequent desiccation in Owens Lake. They found

that concentrations of all the major ions, except  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , increased as the lake continued to desiccate. Calcium and Mg concentrations were controlled by precipitation of carbonate minerals. The brine pool in Owens Lake is dominated by sodium salts of carbonate, sulfate, and chloride (Friedman et al., 1976). All of our groundwater samples were undersaturated with respect to halite (NaCl) and other Cl-bearing evaporite minerals. Thus, chloride was used as a conservative tracer in this study. Sulfate and Cl concentrations in shallow groundwater were strongly correlated ( $r^2=0.91$ ,  $n=15$ ) (Fig. 3; Table 2). However, the scatter around the regression line suggests that the increase in sulfate concentration in groundwaters may occur by mechanisms other than evaporation alone.

The majority of the Eh values in the shallow groundwater were in the range −240 to −170 mV (Fig. 2), consistent with the range expected for sulfate reduction (Schlesinger, 1997). It appears that Eh values are poised within the sulfate reduction zone due to the high sulfate concentrations in shallow groundwater (Ryu et al., 2004). Eh values tend to be higher near the historic shoreline consistent with recharge by oxic surface and groundwater inflows from the surrounding mountains.

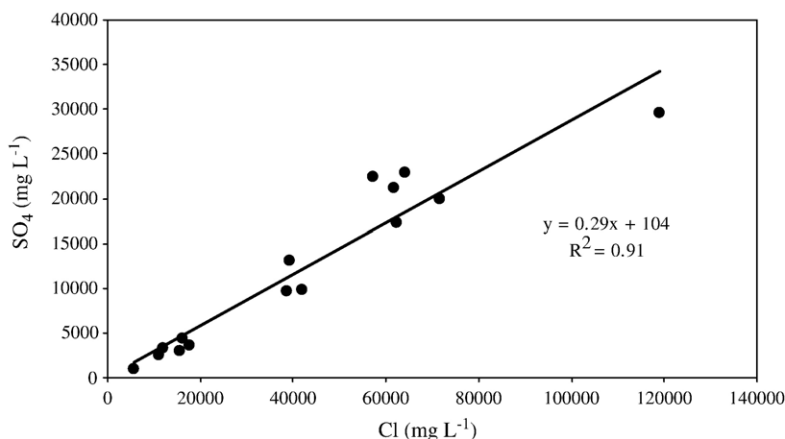


Fig. 3. Plot of dissolved sulfate concentrations vs. chloride concentrations in the shallow groundwater of Owens Lake.

#### 4.2. Sulfur-bearing phases in sedimentary layers

Organic sulfur concentrations in our samples were less than  $100 \text{ mg S kg}^{-1}$ , which are consistent with results from a previous Owens Lake sediment core that showed organic sulfur concentrations were less than  $600 \text{ mg S kg}^{-1}$  (Tuttle, 1993). Surface crust and sediments from the unsaturated zone (0 to  $\sim 20 \text{ cm}$  depth) have the highest content of sulfate mineral phases. Large amounts of sulfate salts are present in the surface crust. A study by Tuttle (1993) indicated that, in most cases, gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) and/or mirabilite ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ) were the dominant sulfate minerals in Owens Lake oxic sediments. The fractions

of sulfate measured near the groundwater zone include a small amount of sulfate from residual porewater. The concentrations of AVS and pyrite were at trace levels or less than detection ( $<100 \text{ mg S kg}^{-1}$ ) in the surface crust and unsaturated zones.

Low Eh values ( $<-200 \text{ mV}$ ), a  $\text{H}_2\text{S}$  odor and jet-black color attributable to sulfides were prevalent throughout the capillary fringe and groundwater zones suggesting that bacterial sulfate reduction occurs along the entire transect from the shoreline to lakebed center. Pyrite was the predominant sulfur-bearing phase in the capillary fringe and groundwater zones where anoxic conditions persisted (Fig. 4). Concentrations of sulfide phases were generally less than  $6 \text{ g S kg}^{-1}$  with pyrite

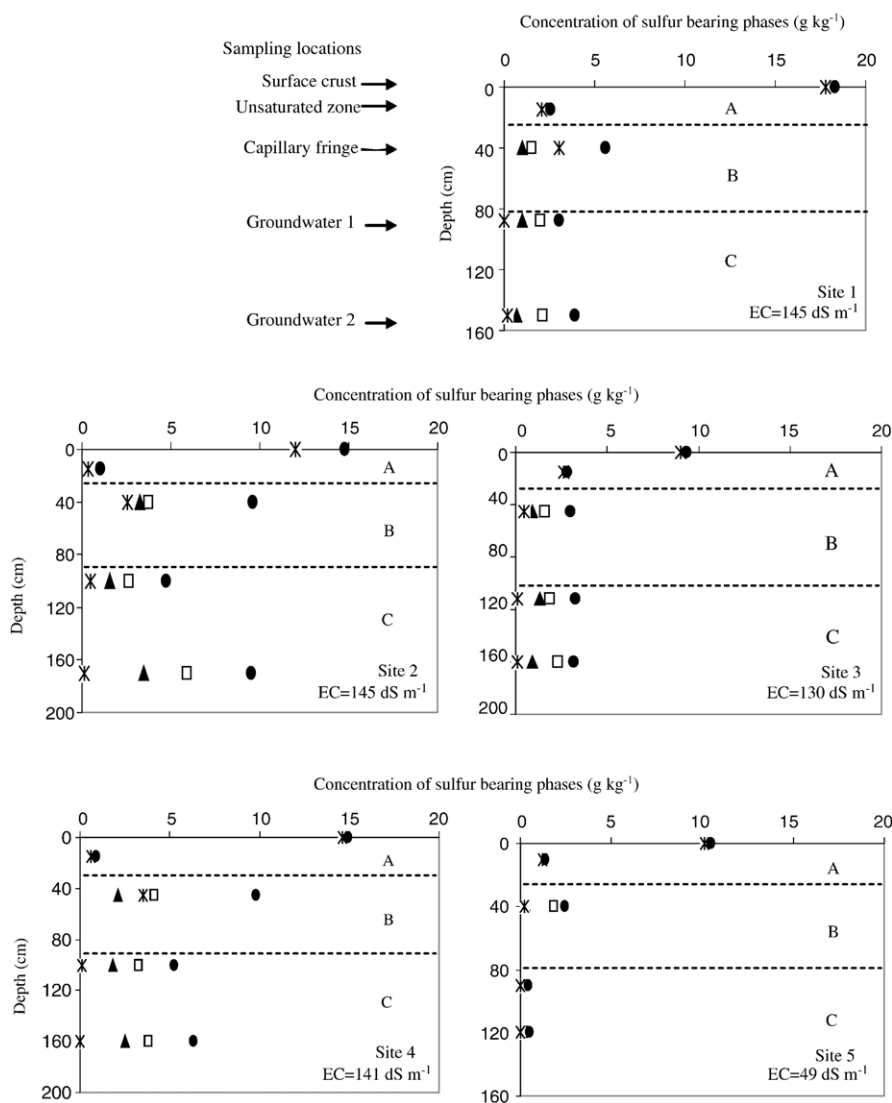


Fig. 4. Concentrations ( $\text{g kg}^{-1}$ ) of pyrite ( $\square$ ), acid volatile sulfide ( $\blacktriangle$ ), sulfate mineral phase ( $\times$ ), and total sulfur ( $\bullet$ ) at different depths (cm) at sites 1–5. Soil profile in the sedimentary layers was divided into unsaturated zone (A), capillary fringe (B), and groundwater zone (C).



concentrations consistently about twice those of AVS throughout the entire profile. Sulfide phases were exceptionally low at site 5, the site nearest the shoreline and having the lowest EC along the transect.

The lower concentration of AVS compared to pyrite is not surprising because AVS phases are metastable relative to pyrite in the presence of excess hydrogen sulfide (Mossmann et al., 1991). Predictions based on the thermodynamic data of Langmuir (1997; Table 1) and the chemical equilibrium model SOLMINEQ.88 are consistent with supersaturation with respect to all iron sulfide minerals in this system. The equilibrium calculations (Table 1) indicate that all groundwaters are supersaturated with respect to mackinawite (FeS) and greigite (Fe<sub>3</sub>S<sub>4</sub>), which are intermediate AVS phases involved in the formation of sedimentary pyrite (Berner, 1970, 1984). The calculations also indicate that groundwaters are highly supersaturated with respect to pyrite (FeS<sub>2</sub>).

Lower concentrations of AVS and pyrite were present at site 5, which has lower EC values and concentrations of dissolved sulfate and sulfide relative to other sites (Fig. 4). The lower EC and sulfate concentrations suggest that site 5 was influenced by subsurface water inflows and was not as strongly evapoconcentrated as the sites nearer the center of the lakebed. In contrast, measured redox was similar at all five sites (Eh range –228 to –200 mv) along the transect (Table 2). The lower dissolved sulfide concentration in groundwater at site 5 corresponds with a low concentration of iron sulfide minerals in the sediment (Table 2).

Low concentrations of dissolved iron and high concentrations of dissolved sulfide have been observed where iron sulfide formation is limited by availability of reactive iron (e.g., Middelburg, 1991; Lyons and Berner, 1992; Henneke et al., 1997; Suits and Wilkin, 1998). In sediments with low Fe availability, sulfide will not be removed by precipitation with Fe(II) resulting in sulfide accumulation in the aqueous phase. H<sub>2</sub>S that is not removed from solution by iron sulfide precipitation is susceptible to oxidation to intermediate oxidation states that can favor the conversion of AVS to pyrite (Mossmann et al., 1991). The low concentration of dissolved iron (<0.05 mg L<sup>-1</sup>) and high concentration of dissolved sulfide in groundwater at the 5 sites (site 1–5; Table 2) may suggest that iron sulfide formation (generally less than 6 g S kg<sup>-1</sup>) is limited by availability of reactive iron. This result is consistent with the previous study (Ryu et al., 2004) indicating that manganese and iron oxyhydroxides (forms most available for reduction) were depleted in groundwater zones, where sulfate reduction was predominant. However, it is difficult to interpret the range of iron sulfide

concentrations shown in Fig. 4 without knowing the source of iron and the reactivity of iron sources with the available sulfide.

#### 4.3. Sulfur isotope composition in sediments

The  $\delta^{34}\text{S}$  values of sulfate mineral phases (with traces of interstitial sulfate) and pyrite/AVS were relatively constant with depth (Fig. 5). There is a slight tendency for  $\delta^{34}\text{S}$  of sulfate mineral phases to increase down core, but the magnitude of the increase is small. The increase is consistent with active sulfate reduction occurring in the deeper anoxic zone. Most of the sulfate  $\delta^{34}\text{S}$  values measured in samples taken in the oxic zone just above the capillary fringe show a slight decrease from values measured above or below. This suggests that a minor amount of isotopically light sulfide diffusing upward from the underlying sediment is being oxidized to sulfate near this boundary.

The near uniformity of isotopic composition of sulfate mineral phases and pyrite/AVS at different depths in Owens Lake sediments contrasts with what is frequently observed in other anoxic systems. Trends in isotopic composition reflect the degree of isolation of the reaction system (i.e., closed/open system). In sediments where the rate of sulfate reduction and precipitation of iron sulfide exceeds the rate of diffusion, the sedimentary porefluids becomes progressively depleted with dissolved sulfate. With continued sulfate reduction and corresponding sulfate depletion, the remaining sulfate and sulfide in the system become progressively enriched in <sup>34</sup>S. This “closed system” effect is frequently observed in association with down-core isotopic trends for iron sulfides in marine sediments (Goldhaber and Kaplan, 1980; Canfield et al., 1992).

The near uniformity of isotopic trends for iron sulfides and sulfate mineral phases with depth at Owens Lake suggests that the sedimentary pore fluids were not significantly depleted in dissolved sulfate, and that sulfate availability did not limit the extent of microbial degradation of organic matter. Evaporative concentration of shallow groundwaters/surface water would lead to vertical density instabilities and encourage vertical mixing between shallow groundwaters and fresher (and less-dense) groundwaters found below (Font, 1995). Studies indicate that the physical instability initiates vertical convection of dense evapoconcentrated brines and the process has been suggested as a transport mechanism (Duffy and Al-Hassan, 1988; Ferguson et al., 1992). The level of instability is influenced by the difference in density between the two fluids, the evaporation rate, and the hydraulic conductivity of the sedi-

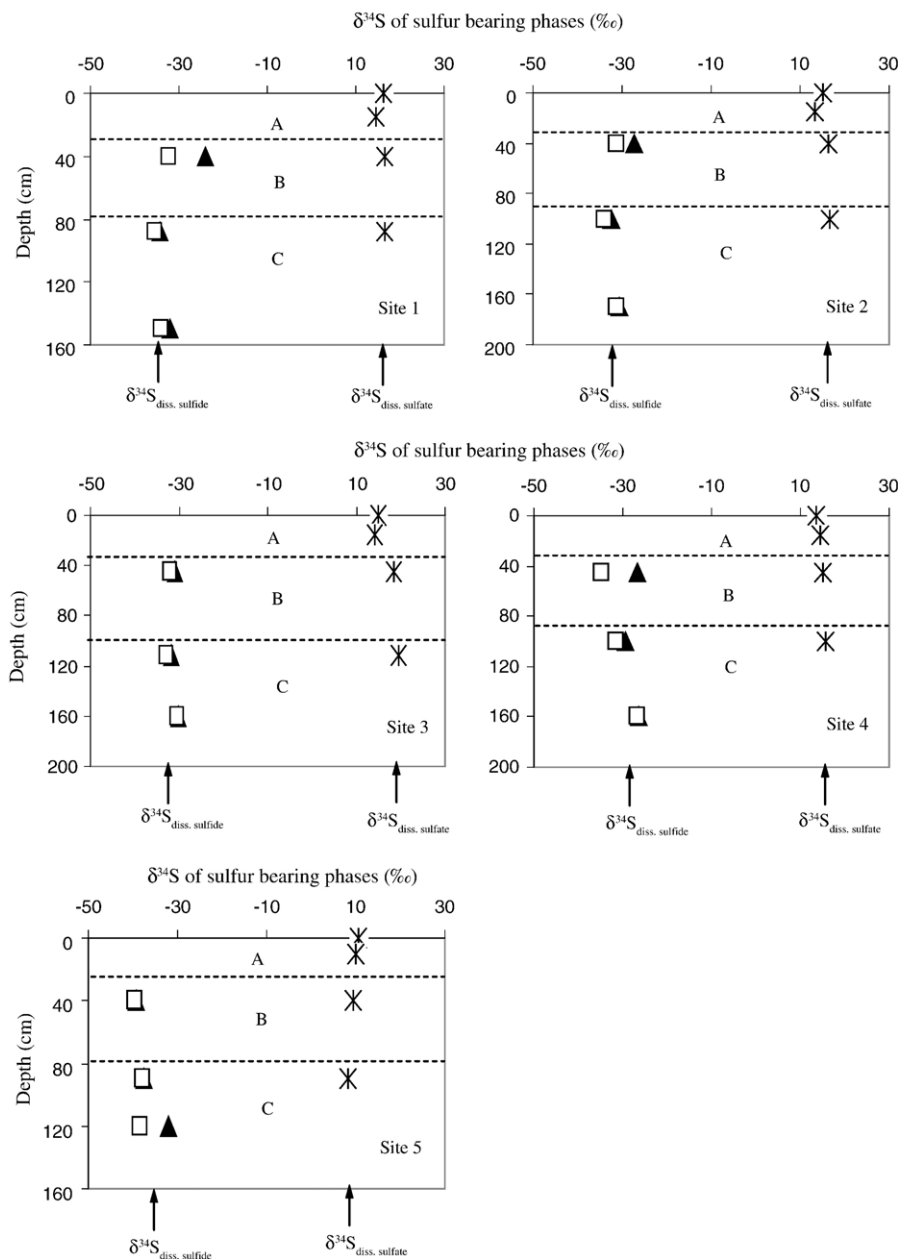


Fig. 5. Isotopic composition ( $\delta^{34}\text{S}$ ) of pyrite (□), acid volatile sulfide (▲), and sulfate mineral phases (✕) at different depths at sites 1–5. The arrows (↑) represent the values of  $\delta^{34}\text{S}$  of dissolved sulfate and sulfide in the groundwater. Soil profile in the sedimentary layers was divided into unsaturated zone (A), capillary fringe (B), and groundwater zone (C).

ments (Ferguson et al., 1992). Higher permeability sediment (sand) found near the margins of the lake bed would be more conducive to the initiation of convective mixing due to density instability compared with the more clay-rich sediment that dominates the central lakebed region (Font, 1995). Occasional inundation of the lake surface by the Owens River (e.g., Friedman et al., 1976) or heavy rainfall result in dilution of the

surface brines and change the density stratification of the shallow groundwaters.

Experimental results indicate that  $\delta^{34}\text{S}$  values of the AVS are controlled by the  $\delta^{34}\text{S}$  of  $\text{HS}^-$  (Price and Shieh, 1979; Mossman et al., 1991). The studies also indicate that a small fractionation can be observed in the metal sulfides compared to  $\text{HS}^-$  depending on the precipitation conditions. Fig. 5 shows that the  $\delta^{34}\text{S}$  of AVS at

Table 2  
Geochemical data for Owens Lake groundwater and sediment samples

ID	pH	EC (dS m <sup>-1</sup> )	Eh (mV)	Na (mg L <sup>-1</sup> )	K (mg L <sup>-1</sup> )	Ca (mg L <sup>-1</sup> )	Mg (mg L <sup>-1</sup> )	Cl (mg L <sup>-1</sup> )	Sulfate (mg L <sup>-1</sup> )	Sulfide (mg L <sup>-1</sup> )	B (mg L <sup>-1</sup> )	Fe(II) (mg L <sup>-1</sup> )	DOC (mg L <sup>-1</sup> )	OM (mg L <sup>-1</sup> )	Alkalinity (mg CaCO <sub>3</sub> L <sup>-1</sup> )
1	9.4	145	-228	93,670	6486	334.0	75.8	64,065	22,946	134.7	1312	0.04	299.6	14.2	59,450
2	9.4	147	-200	83,204	7005	382.0	83.2	57,209	22,392	101.0	1401	0.03	215.1	15.6	65,950
3	9.5	127	-212	67,398	5495	289.0	60.4	39,221	13,024	112.2	1033	0.05	215.1	9.5	51,260
4	9.5	135	-214	88,046	5929	305.0	68.3	62,352	17,337	67.3	1132	0.04	226.3	8.7	56,960
5	9.6	47	-216	17,686	1594	190.2	40.3	11,992	3316	56.1	233	0.03	82.1	7.8	14,250
11	9.3	44	-26	13,860	1095	308.6	55.9	11,007	2543	4.8	173	0.42	32.1	1.1	11,330
12	9.3	63	-104	24,476	1896	60.1	7.3	16,285	4413	17.6	346	3.56	45.7	1.3	18,810
13	9.5	69	-187	21,108	2166	76.2	21.9	15,590	3025	46.5	368	0.47	35.4	2.1	19,040
14	9.4	61	-206	21,731	1783	64.1	9.7	17,802	3549	36.9	357	1.45	35.2	3.0	14,530
15	9.4	25	-163	7586	848	24.0	7.3	5583	999	36.9	101	8.90	30.2	1.5	5530
16	9.3	107	-213	53,936	4429	104.2	19.4	38,816	9668	36.9	649	0.18	82.8	4.7	35,810
17	9.4	119	-213	58,262	5911	116.2	14.6	41,850	9769	35.3	692	0.30	79.7	3.7	37,980
18	9.1	158	-206	136,264	9746	284.6	55.9	119,082	29,551	48.1	1608	0.47	191.4	4.9	71,310
19	9.1	149	-192	101,211	7690	232.5	58.3	71,687	19,941	35.3	1586	0.12	174.6	14.6	73,520
20	9.0	151	-239	91,076	6978	460.9	87.5	61,875	21,139	118.6	1521	0.09	141.1	5.8	67,530

different depths were similar to the  $\delta^{34}\text{S}$  of dissolved sulfide of groundwater at each site. The difference between  $\delta^{34}\text{S}$  of AVS and  $\delta^{34}\text{S}$  of pyrite in these sediments is generally less than 3‰ (Fig. 5) suggesting fast conversion of AVS to pyrite (Price and Shieh, 1979). However, some differences were observed in a few samples, which might indicate the conversion of AVS to pyrite locally involves disproportionation of sulfur compounds with intermediate oxidation states.

#### 4.4. Sulfur isotope composition of shallow groundwater

Samples with chloride concentrations in the pore waters higher than about 4000 mg L<sup>-1</sup>, those which have undergone the most evaporative concentration, show a relatively small range in  $\delta^{34}\text{S}$  of dissolved sulfate ( $\delta^{34}\text{S}_{\text{diss. sulfate}}$ ) values between 16.2‰ and 19.2‰ (Fig. 6). Samples with lower chloride concentrations show more variability. The initial sulfur isotope value of sulfate entering Owens Lake is not well constrained. A  $\delta^{34}\text{S}_{\text{sulfate}}$  value of +8.5‰ was measured in the Owens River in 1962 (Holser and Kaplan, 1966), and a  $\delta^{34}\text{S}_{\text{sulfate}}$  value of near +7‰ from atmospheric (or meteoric) sulfur was measured in Death Valley (Yang et al., 1997). These values might be representative of  $\delta^{34}\text{S}_{\text{diss. sulfate}}$  for Owens Lake inflow. The variability of  $\delta^{34}\text{S}_{\text{diss. sulfate}}$  in lower Cl waters likely represents mixing between inflows and brines in Owens Lake, combined with variations in the extent of sulfate reduction and sulfide oxidation. The more constant range of  $\delta^{34}\text{S}_{\text{diss. sulfate}}$  values in groundwaters with higher Cl concentration indicates that the influence from groundwater mixing was limited toward the center of the lakebed and the central brine mass is relatively homogeneous.

Table 3 and Fig. 7 show that the difference in the S-isotopic compositions of dissolved  $\text{SO}_4^{2-}$  and total reduced sulfur ( $\Delta^{34}\text{S} = \delta^{34}\text{S}_{\text{diss. sulfate}} - \delta^{34}\text{S}_{\text{total reduced sulfur}}$ ) is also relatively constant (42.1–52.7‰) in those samples with the highest salinity. The isotopic difference between sulfate and sulfide in lower salinity samples shows more variability (23.6–47.0‰) and tends to show less fractionation. Rees (1973) and Rye et al. (1981) reported that isotopic fractionation ( $\Delta^{34}\text{S}$ ) increases as the rate of sulfate reduction decreases because sulfate reducers can be more selective in their use of  $^{32}\text{S}$ . Thus, the large differences between  $\delta^{34}\text{S}_{\text{diss. sulfate}}$  and  $\delta^{34}\text{S}_{\text{total reduced sulfur}}$  at high Cl concentration might suggest a comparatively low net specific rate of sulfate reduction at these sites. However, experimental results of isotope fractionation during dissimilatory sulfate reduction by pure cultures have shown variable,

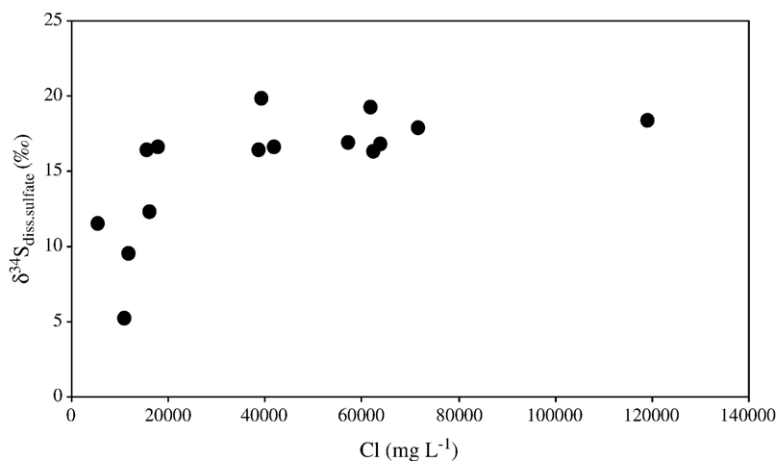


Fig. 6. Plot of  $\delta^{34}\text{S}$  of dissolved sulfate vs. chloride concentration in groundwater.

but generally lower degrees of isotopic fractionation (Kemp and Thode, 1968; Chambers et al., 1975).

The degree of isotope fractionation and the rate of sulfate reduction may be controlled by temperature, sulfate concentration, and the availability of reactive (microbially labile) organic matter (Kaplan and Rittenberg, 1964; Kemp and Thode, 1968). Temperatures at the depth of the sulfate reduction zone are relatively constant ( $\sim 20^\circ\text{C}$ ) and sulfate concentrations are too high to limit sulfate reduction at Owens Lake. Thus, temperature and sulfate concentrations do not appear to

be factors that strongly control isotopic fractionation of sulfur in Owens Lake groundwaters and sediments. Some studies have found that the rate of reduction and the magnitude of the isotopic fractionation also depend on the nature of organic substrates (electron donor) (Kaplan and Rittenberg, 1964; Goldhaber and Kaplan, 1975; Berner, 1984; Fry et al., 1995). When organic substrates become limiting to sulfate reduction, rates of sulfate reduction slow resulting in greater isotopic fractionation (Canfield, 2001). Similarly, the types of organic substrates utilized for sulfate reduction can affect sulfur fractionation (Detmers et al., 2001). For example, acetate, which is known to provide lower energetic yields for sulfate reduction, generally results in greater isotopic fractionation (Detmers et al., 2001). In contrast, substrates such as lactate, which provide greater energetic yields, generally result in lower isotopic fractionation (Detmers et al., 2001). In our study, individual organic compounds were not determined and there was no significant correlation between bulk dissolved or particulate organic matter and isotopic fractionation.

Because the isotope fractionation between sulfate and total reduced sulfur was generally greatest in the samples with the highest chloride, which is closely related to salinity (Fig. 7), we consider the possibility that high salinity may limit the activity of sulfate reducing bacteria. Although a large variety of halophilic or halotolerant bacteria are found in brines, sulfate reduction rates have previously been found to be inversely proportional to salinity (Ollivier et al., 1994; Sørensen et al., 2004). Thus, we cannot preclude salinity as an additional factor controlling the specific rate of sulfate reduction and isotope fractionation in groundwaters and sediments of Owens Dry Lake.

Table 3

Sulfur isotope ratios of dissolved sulfate ( $\delta^{34}\text{S}_{\text{diss. sulfate}}$ ), pyrite ( $\delta^{34}\text{S}_{\text{pyrite}}$ ), and total reduced sulfur ( $\delta^{34}\text{S}_{\text{total reduced sulfur}}$ ) and isotope fractionation between sulfate and total reduced sulfur ( $\delta^{34}\text{S}_{\text{diss. sulfate}} - \delta^{34}\text{S}_{\text{total reduced sulfur}}$ ) in groundwater

ID	EC ( $\text{dS m}^{-1}$ )	$\delta^{34}\text{S}_{\text{diss. sulfate}}$ (‰)	$\delta^{34}\text{S}_{\text{pyrite}}$ (‰)	$\Delta^{34}\text{S}_{\text{diss. sulfate}} - \delta^{34}\text{S}_{\text{total reduced sulfur}}$ (‰)
1	145	16.7	−35.4	52.2
2	147	16.9	−34.0	50.8
3	127	19.8	−32.9	52.7
4	135	16.2	−31.6	47.8
5	47	9.5	−37.5	47.0
			$\delta^{34}\text{S}_{\text{total reduced sulfur}}$	
11	44	5.1	−18.5	23.6
12	63	12.3	−16.1	28.3
13	69	16.4	−16.1	32.6
14	61	16.6	−15.1	31.7
15	25	11.5	−16.1	27.6
16	107	16.4	−29.7	46.1
17	119	16.5	−27.2	43.7
18	158	18.3	−23.7	42.1
19	149	17.8	−25.5	43.4
20	151	19.2	−31.6	50.8

From sites 1–5,  $\delta^{34}\text{S}_{\text{pyrite}}$  was used as  $\delta^{34}\text{S}_{\text{total reduced sulfur}}$ , which is mainly acid volatile sulfides and pyrite.

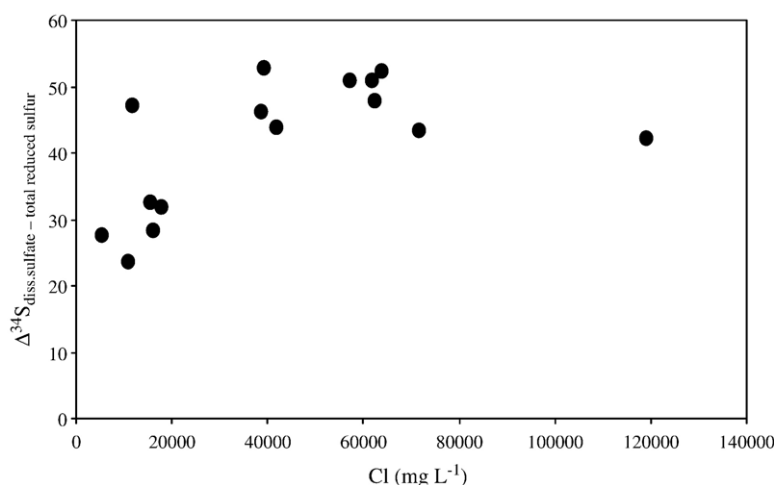
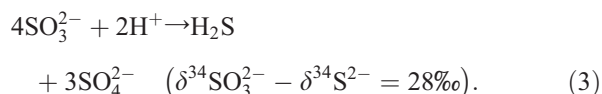
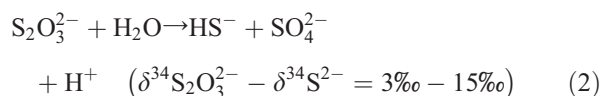
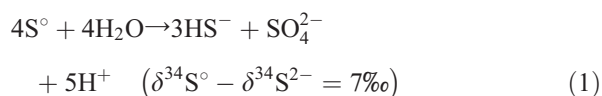


Fig. 7. Plot of isotope fractionation between dissolved sulfate and total reduced sulfur vs. chloride concentration in groundwater.

The large fractionation measured in Owens Lake sediments likely indicates additional fractionation created during sulfide oxidation followed by disproportionation of intermediate sulfur compounds (Jørgensen, 1990; Canfield and Thamdrup, 1994; Canfield and Teske, 1996; Habicht and Canfield, 2001). Repeated sulfide oxidation to  $S^0$  and other sulfur intermediates, followed by disproportionation can produce sulfide more depleted in  $^{34}S$  than bacterial sulfate reduction alone (Habicht and Canfield, 2001). Sulfide can be oxidized and produce various intermediate sulfur compounds, such as,  $S^0$ ,  $S_2O_3^{2-}$ , and  $SO_3^{2-}$  (Kelly, 1988; Habicht and Canfield, 1997). Small fractionations are associated with the oxidation of reduced sulfur compounds directly to sulfate (Fry et al., 1986; Habicht et al., 1998). However,  $^{34}S$ -depleted sulfides are produced during the microbial disproportionation of  $S^0$ ,  $S_2O_3^{2-}$ , and  $SO_3^{2-}$  (Canfield and Thamdrup, 1994; Canfield et al., 1998; Cypionka et al., 1998; Habicht et al., 1998). Habicht and Canfield (2001) determined the isotopic fractionation generated by disproportionation of these intermediate sulfur compounds:



Aller and Rude (1988) indicate that  $O_2$ ,  $NO_3^-$ , or Fe(III) and Mn(IV) compounds are among the potential oxidants of sulfide in the sediment. They also showed that iron oxides are less efficient than manganese oxides in the oxidation of sulfide to sulfate, although iron oxides are generally much more abundant than manganese oxides (Aller and Rude, 1988). In unsaturated zones where gases exchange freely with the atmosphere, oxygen is likely participating in sulfide oxidation of the sediments at Owens Lake. The intermediate sulfur compounds can be formed by sulfide oxidation at the interface between oxic and anoxic layers, as oxygen penetrates from the lakebed surface towards groundwaters. The slight decrease in  $\delta^{34}S_{\text{sulfate mineral phase}}$  observed in some cores at the top of the capillary fringe zone suggests that this is the dominant pathway of sulfide oxidation at Owens Lake.

## 5. Conclusions

This study describes the distribution of sulfur and S-isotopes in surface sediments and shallow groundwaters of Owens Dry Lake. Pyrite was the predominant sulfur-bearing phase in the anoxic capillary fringe and groundwater zones. The high concentrations of dissolved sulfide and low concentrations of dissolved Fe suggest that the availability of reactive Fe limits formation of iron sulfides. The enrichment of  $\delta^{34}S_{\text{sulfate}}$  and the existence of  $^{34}S$  depleted sulfides provide evidence of bacterial sulfate reduction in the groundwater/sediments. The uniformity of isotopic trends for sulfur bearing mineral phases with depth in the sedimentary layers suggests that the groundwater and sediments are an open system with respect to the availability of sulfate. The vertical mixing initiated by instability of water density due to



evaporation between upper and lower sedimentary layers is likely to promote convective mixing in the sediment and provides an additional mechanism to diffusion to ensure adequate sulfate supply in the sediment. The isotopic signature of sediments indicates a strong connection between the isotopic composition of dissolved sulfate and sulfide in groundwater and the isotopic composition of their mineral phases above the groundwater. Therefore, the presence of shallow groundwater that is connected to the atmosphere through vertical mixing and evaporation is an important factor regulating sulfur biogeochemistry in the sediment layers. There is more variability in the isotope fractionation ( $\Delta^{34}\text{S}$ ) between sulfate and total reduced sulfur in sediments with the lowest salinity groundwaters. At higher salinities, with corresponding high sulfate concentrations, the isotopic fractionation is relatively constant at values that approach or exceed the largest fractionations observed in laboratory experiments using cultured bacteria. The large degree of fractionation observed suggests that cycling of sulfur by repeated oxidation/reduction involving intermediate oxidation state compounds subject to disproportionation reactions is occurring in the transition zone from oxic to anoxic conditions in Owens Lake sediment.

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